On the Diffusion Model of Mao and Toor

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Mao and Toor (*4*) successfully verified the experimental data of Vassilatos and Toor (*7*) by using a diffusion model based on simultaneous interdiffusion and reaction between alternate slabs of reactants. Their diffusion model contains D/δ^2 as a parameter where D is the molecular diffusion coefficient and δ is the empirically determined slab thickness. Harris and Srivastava (*2*) and Kattan and Adler (*3*) simulated the reactor of Vassilatos and Toor as a batch reactor consisting of a finite number of fluid elements which were assumed to be coalescing and redispersing at a particular rate. This rate of coalescence was determined by matching a single experimental run. Kattan and Adler varied the coalescence rate as a function of distance along the length of the reactor, to match the experimental conversion data for very rapid reaction at various axial positions in the reactor (see Figure 1). Then other experimental runs for very rapid, rapid, and slow reactions were successfully verified by using the same value of the coalescence rate as a function of axial position. Harris and Srivastava used a constant value of coalescence rate. The recently proposed model of Rao and Dunn (*5*) simulates both axial and radial dispersion in a tubular reactor by using a Monte Carlo coalescence model along the lines suggested by Spielman and Levenspiel (*6*). This model was also found to represent the data of Vassilatos and Toor quite well (*5*).

The slab diffusion model of Mao and Toor suggests that the mixing rate is controlled by molecular diffusion even in a turbulent flow field. On the other hand, the coalescence-dispersion type models [for example, the models of Kattan and Adler (*3*), Harris and Srivastava (*2*), Rao and Dunn (*5*)] imply that turbulent dispersion controls the rate of mixing. The fact that both types of models agree with the experimental data of Vassilatos and Toor lead Mao and Toor to conclude that the reactor conversion is not very sensitive to the details of mixing. Although the two types of models are very different in concept, this communication attempts to show intuitively that the single-slab diffusion model of Mao and Toor and the coalescence-dispersion models are equivalent.

By applying the theory of isotropic turbulence, it can be shown that the decay of root mean square concentration fluctuations of a diffusing species A is given by

$$\frac{d\overline{c^2}}{dt} = -\frac{12\,D}{l_m^2}\,\overline{c^2} \qquad (1)$$

where l_m is the scalar microscale of turbulence.

From the above equation, one can regard D/l_m^2 as a single parameter to describe molecular diffusion. Assuming that turbulence has dispersed the fluid to the fine scale and no longer controls the ultimate molecular mixing and chemical reaction rates, one can conceive a model wherein fluid lumps of size equal to l_m interact with each other purely by molecular diffusion. This is what is simulated in the single-slab diffusion model of Mao and Toor (*4*).

Evangelista, Katz and Shinnar (*1*) derived population balance equations for a batch reactor consisting of a finite number of fluid elements which were assumed to be coalescing and redispersing at a particular rate which in general could be time dependent. They derived the following equation for the decay of variance for a tracer input.

$$\frac{d\sigma^2}{dt} = -\beta\sigma^2 \qquad (2)$$

Where β is the coalescence rate per unit fluid element. They also compared Equations (1) and (2) and arrived at the relationship

$$\beta = \frac{12\,D}{l_m^2} \qquad (3)$$

This comparison is justified when one considers that the Equations (1) and (2) are similar in form. Also, it should be noted that equations for a batch reactor are equivalent to the equations for a plug-flow reactor if time is converted to distance coordinate. In the plug-flow reactor fluid elements coalesce with each other at random at the same axial position. This case corresponds exactly to the model

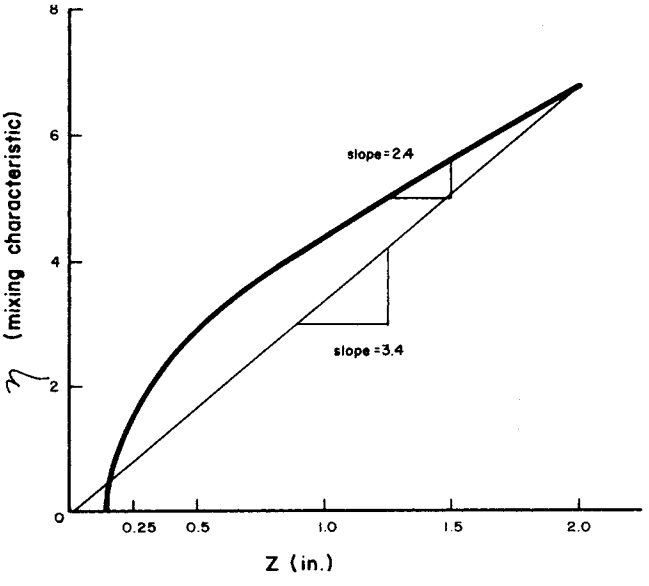

Fig. 1. Mixing characteristic.

of Kattan and Adler. Hence, from Equation (3) it should be possible to calculate D/l_m^2 if β were known.

The value of β, and hence D/l_m^2, at any axial position can be found by multiplying the slope of the plot of η versus Z as shown in Figure 1 (reproduced from the paper by Kattan and Adler) by the velocity of the fluid in the reactor. η is defined as the total number of coalescences experienced by the fluid elements between the entrance and any axial position Z divided by the total number of fluid elements. For example, the slope of the curve is 0 up to a distance of about 0.15 in. from the inlet, then it rises very sharply and reaches a constant value. If one calculates D/l_m^2 from this constant value of slope, D/l_m^2 turns out to be 3.25 (velocity of fluid in the reactor is taken as 16 in./sec.). However, if one assumes a straight line relationship from the origin to the ordinate, at Z = 2.0 in., the value of D/l_m^2 turns out to be 4.53 which is exactly the same value used for D/δ^2 in the single-slab diffusion model of Mao and Toor. This suggests the equivalence between the slab-diffusion model and the coalescence dispersion model for a very rapid second order reaction with unmixed feed or a tracer mixing process in a tubular reactor.

As can be seen in the differential equation model of Mao and Toor and in the coalescence-dispersion models, the reaction terms do not interact with diffusion terms and hence the equivalence ought to remain valid for any value of the reaction rate constant. That is, the mixing as depicted in the model is unaffected by the chemical reaction. Of course both types of models do represent the experimental data of Vassilatos and Toor for all reaction rates.

ACKNOWLEDGMENT

The authors are grateful for a National Science Foundation grant (GK-10043) which supported this work.

NOTATION

$\overline{c^2}$ = mean square concentration fluctuation
D = molecular diffusion coefficient
l_m = scalar microscale of turbulence
N = number of drops in the reactor
t = time
Z = axial position (inches)

Greek Letters

β = coalescence rate per unit fluid element
δ = slab thickness
σ^2 = variance of tracer concentration distribution
η = mixing characteristic, dimensionless

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An Experimental Investigation of a Porous Medium Model with Nonuniform Pores

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Many techniques have been employed to describe mathematically the flow of fluids in porous media (*1*). In the majority of cases only one particular phenomenon was investigated. An expression for the particular property is usually derived empirically and contains a term characteristic of the medium. These tortuosity and heterogeneity factors have been derived for a number of types of porous media (*2*).

To study the microstructure of porous media and its effect on the observable bulk properties more systematically, several statistical models have been postulated. One of the first models was that of a bundle of straight capillary tubes; another depicted the medium as a series of mixing cells. Both have been used successfully to a degree, even though they are simple models. Although the void spaces in most cases can be visualized as capillaries, their arrangement is highly disordered, and the sizes of the voids are definitely nonuniform. Fatt (*3*) has constructed network models which include nonuniformity to predict permeability and capillary pressure. De Josselin De Jong (*4*) and Saffman (*5*) postulated random network models with uniform properties to predict the dispersion in such models. Haring and Greenkorn (*6*) postulated a statistical model which includes nonuniformity by allowing pore radii and pore lengths to be distributed. They have calculated the properties of such a model by fitting the radii and lengths with two parameter distribution functions. These parameters are related to the first and second moments of the microstructure of the medium. Equations for the various flow properties of the medium have been derived by integrating over joint distributions of the models.

This presents an experimental investigation of the measurement of certain properties of a porous medium to

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